

PRODUCTION OF POLYCRYSTALLINE SILICON INGOT

Publication number: JP11092129 (A)

Also published as:

Publication date: 1999-04-06

JP3571507 (B2)

Inventor(s): NATSUME YOSHITAKE; ONIZUKA TOSHIHIRO +

Applicant(s): SUMITOMO SITIX AMAGASAKI KK +

Classification:

- international: C01B33/02; C30B29/06; H01L31/04; C01B33/00; C30B29/06;
H01L31/04; (IPC1-7): C01B33/02; C30B29/06; H01L31/04

- European:

Application number: JP19970253445 19970918

Priority number(s): JP19970253445 19970918

Abstract of JP 11092129 (A)

PROBLEM TO BE SOLVED: To produce a polycrystalline silicon ingot for a solar cell adaptable to reduction in cost without deteriorating meltability even when fine silicon powder is used. SOLUTION: Silicon powder is granulated by high pressure compacting and the resultant granulated silicon green compacts are used as starting material to be melted to cast the objective ingot. The granulated silicon green compacts are preferably dried and/or sintered and the diameter of the compacts is preferably regulated to 1-10 mm.

Data supplied from the **espacenet** database — Worldwide

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平11-92129

(43)公開日 平成11年(1999)4月6日

(51)Int.Cl.⁶
C 01 B 33/02
C 30 B 29/06
H 01 L 31/04

識別記号

F I
C 01 B 33/02 E
C 30 B 29/06 D
H 01 L 31/04 H

審査請求 未請求 請求項の数3 OL (全 6 頁)

(21)出願番号 特願平9-253445

(22)出願日 平成9年(1997)9月18日

(71)出願人 397064944
株式会社住友シチックス尼崎
兵庫県尼崎市東浜町1番地

(72)発明者 夏目 義丈
兵庫県尼崎市東浜町1番地住友シチックス
株式会社内

(72)発明者 鬼塚 智弘
兵庫県尼崎市東浜町1番地住友シチックス
株式会社内

(74)代理人 弁理士 森 道雄 (外1名)

(54)【発明の名称】 多結晶シリコンインゴットの製造方法

(57)【要約】

【課題】細粒のシリコン粉末であっても、溶解性を損なうことなく、低価格化に対応した太陽電池用の多結晶シリコンインゴットを製造する。

【解決手段】シリコン粉末を高圧成形で造粒してのち、この造粒されたシリコン圧粉体を溶解原料としてインゴットを鋳造することを特徴とする多結晶シリコンインゴットの製造方法である。上記の製造方法において、造粒されたシリコン圧粉体を乾燥または／および焼結するのが望ましく、さらに、溶解原料となるシリコン圧粉体の粒径を1mm～10mmにするのが望ましい。

【特許請求の範囲】

【請求項1】シリコン粉末を高圧成形で造粒してのち、この造粒されたシリコン圧粉体を溶解原料としてインゴットを鋳造することを特徴とする多結晶シリコンインゴットの製造方法。

【請求項2】造粒されたシリコン圧粉体を、乾燥または／および焼結することを特徴とする請求項1記載の多結晶シリコンインゴットの製造方法。

【請求項3】溶解原料となるシリコン圧粉体の粒径を1mm～10mmにすることを特徴とする請求項1または請求項2に記載の多結晶シリコンインゴットの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、太陽電池用に用いられる多結晶シリコンインゴットを製造する方法に関するもので、さらに詳しくは高純度シリコンの製造とともに生成されるシリコン粉末を造粒し、この圧粉体を溶解原料とする多結晶シリコンインゴットの製造方法に関するものである。

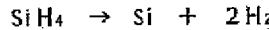
【0002】

【従来の技術】最近の太陽光発電の普及にともない、太陽電池の製造技術は半導体用シリコン、アモルファスシリコン、多結晶シリコン等と多様な分野で適用され、いずれの分野においても技術開発は著しい。開発当初の太

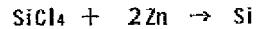


しかしながら、このシーメンス法では、多結晶シリコン心棒の加熱に多くの電力を消費することから電力原単位が悪くなる。さらに反応炉に導入されたトリクロロシランのうち僅かの比率しか多結晶シリコンの生成に寄与しないので、生産効率が著しく低い。このため、この製造方法は、低価格化を指向する太陽電池用シリコン原料の製造方法として適さない。

【0005】そこで、シーメンス法とは全く異なる粒状



シーメンス法におけるシリコン心棒に比べ、粒状シリコンの総面積は圧倒的に大きいので、流動床反応炉内での多結晶シリコンの生成効率が高い。さらに、流動造粒法によって製造された多結晶シリコンの純度はシーメンス法のそれと比べ同等であるが、消費エネルギーは1/5から1/10程度にまで低減させることができるとともに、設備投資を半減させることができる。このような観点から、流動造粒法は、太陽電池用シリコン原料の製造方法として有効な方法であるといえる。



亜鉛還元法は、上記(C)式に示すように、金属シリコンを塩化処理(ハロゲン化反応)して中間化合物を生成したのち、それを2次汚染されることなく還元・分解して製造する方法であるから、高純度シリコンの製造に適する。一方、ほぼ全ての四塩化珪素(SiCl₄)がシリコン(Si)に進行する反応系であるから反応効率に優れ、

陽電池に要求された特性は光電変換効率の向上を主眼とする高性能化であったが、太陽電池の普及とともにあって低価格化が指向されるようになってきた。このため、例えば、多結晶シリコン基板の製造において、原料に半導体用シリコンとして製造された多結晶シリコンの格外品や単結晶シリコンの残材等を破碎洗浄して使用されるようになる。ところが、半導体用シリコンの品種が多種にわたるので一定品質のものが確保できない、あるいは太陽電池の生産量に応じた数量を安定して確保できない等の理由から、低価格化にも限界がある。このため、今後の太陽電池の開発には、所定の光電変換効率を発揮する高純度の品質と低成本化に対応したシリコンの製造技術の確立が必要になる。

【0003】従来から高純度の多結晶シリコンを製造する方法として、シーメンス法(Siemens Method)がある。この方法は、中間化合物であるトリクロロシラン(SiHCl₃)を水素(H₂)によって還元する方法であって、気化された高純度のトリクロロシランを高純度の水素とともに反応炉内に導入し、トリクロロシランを下記(A)の反応式にしたがって分解させ、両端をグラファイト電極で支えられ約1100℃に加熱された多結晶シリコン心棒の表面に多結晶シリコンを気相成長させるものである。

【0004】



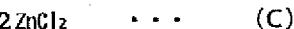
の多結晶シリコンを生成するプロセスとして、流動造粒法が開発された。この製造方法では、流動床反応炉が用いられ、反応炉内にシードとなるシリコン微粉末を流動させておき、その中にモノシラン(SiH₄)と水素の混合ガスとが導入され、600～700℃に加熱された流動雰囲気中でモノシランが分解する。このとき下記(B)の反応式を経て粒状の多結晶シリコンが生成する。

【0006】



【0007】さらに、反応効率に優れた多結晶シリコンの製造法として、いわゆる「四塩化珪素の亜鉛還元法」(以下、単に「亜鉛還元法」という)が、太陽電池用シリコン原料の製造方法として採用されるようになってきた。この製造方法は、下記(C)の反応式で示されるように、中間化合物として四塩化珪素(SiCl₄)を用い、これを溶融亜鉛(Zn)で還元することによって多結晶シリコンを製造する方法である。

【0008】



生産効率のよい製造方法であり、製造コストの面において有利な製造方法である。

【0009】図1は、亜鉛還元法による多結晶シリコンの製造工程の一例を説明する図である。同図から明らかに、この亜鉛還元法では、反応原料(SiCl₄およびZn)の供給工程、還元工程、副生成物の分離工程およ

び高純度シリコン (Si) の取り出し工程と大きく区分される。

【0010】反応原料を供給工程では、原料として、金属シリコンを塩化処理した四塩化珪素 ($SiCl_4$) と還元剤である金属亜鉛 (Zn) とが準備される。金属亜鉛 (Zn) は、反応炉への供給を容易にするために、450~550 °C の範囲に加熱され溶融状態にされる。一方、中間化合物である四塩化珪素 ($SiCl_4$) は常温で収容され、液体状態に保たれる (融点-70°C)。

【0011】還元工程では、中間化合物である四塩化珪素 ($SiCl_4$) を溶融亜鉛 (Zn) で還元することによって、多結晶シリコンと副生成した塩化亜鉛 ($ZnCl_2$) とを得る。このとき、塩化亜鉛の沸点は732°Cであるので、還元反応によって生成した塩化亜鉛 ($ZnCl_2$) は蒸気となり、また、同時に生成される多結晶シリコン粉は非常に微細であり、塩化亜鉛 ($ZnCl_2$) の蒸気とともに還元用の反応炉の外部に排出される。

【0012】副生成物の分離工程では、副生成した塩化亜鉛 ($ZnCl_2$) を分離するため、蒸発分離法または液体過濾法が用いられる。蒸発分離法を用いる場合、多結晶シリコンと塩化亜鉛 ($ZnCl_2$) とからなる混合物が分離容器内に導入され、その後、真空引きとともに加熱され、塩化亜鉛 ($ZnCl_2$) が蒸発・分離されて、多結晶シリコンが回収される。液体過濾法を用いる場合は、分離容器内に高温特性を有し、かつ汚染が少ない多孔質のファインセラミックフィルターが施され、導入された混合物が加圧濾過される。

【0013】高純度シリコンの取り出し工程では、上記の分離を繰り返すことによって、完全に不純物が除去され、充分に高純度化した多結晶シリコンが取り出される。この亜鉛還元法では、上記の反応原料の供給から高純度シリコンの取り出しに至る工程を連続して処理することができるので、一層、生産効率の高い製造方法を提供することができる。

【0014】上述の通り、流動造粒法、亜鉛還元法とも、低コストに対応した生産効率の高い製造方法であり、しかも、2次汚染のおそれもないことから、太陽電池用シリコン原料の製造方法として有効な方法である。

【0015】

【発明が解決しようとする課題】通常、流動造粒法によって製造される粒状の多結晶シリコンは、直径100~150 μm で、平均径が700 μm 程度となる。このとき発生する細粒、例えば直径3 μm 以下の粉末シリコンは、15% 程度発生する。一方、前述の通り、亜鉛還元法では、前記 (C) 式で示すように、四塩化珪素を溶融亜鉛によって還元することによって生成される多結晶シリコン粉末は非常に微細であり、副生成物を分離後取り出されたシリコンはいずれも直径3 μm 以下の細粒のものである。

【0016】図3は、後述する多結晶シリコンインゴットの製造に用いられる電磁誘導による連続铸造装置の概

略構成を示す図である。装置の中心には、互いに電気的に絶縁されるようにセグメントを切った金属製の水冷坩堝 (コールドクルーシブル) が、誘導コイル中に設置されている。そして、磁界を坩堝内に浸透させることによって、磁気圧によって溶融シリコンは無接触で保持されて溶解が行われる。連続的にインゴットを製造するため、誘導コイル中のシリコンインゴットの上端面が溶解され、その上面に形成された溶融シリコンに粒状の溶解原料が供給され、原料の溶解および凝固を繰り返してシリコンインゴットが下方に引き出される。原料溶解中は、装置内の真空引き後、不活性ガス雰囲気に保たれる。

【0017】このとき、溶融シリコンに供給される粒状の溶解原料が細粒、例えば直径1 μm 以下であると、溶融シリコンの表面に浮遊するだけであり、溶融シリコンには溶け込みず、充分な溶解ができない。しかも、不活性ガスの吹き出しやガス流れによって飛散し、装置内のガス吸引不良の要因となる。したがって、流動造粒法によって製造される粒状の多結晶シリコンを溶解原料とする場合には、直径1 μm 以下の細粒シリコンを除去する必要がある。このため、溶解原料コストの上昇が避けられない。また、亜鉛還元法によって生成される多結晶シリコン粉末は、全て直径3 μm 以下の細粒であることから、図3に示すような連続铸造装置では使用できないことになる。

【0018】本発明は、従来の連続铸造法における多結晶シリコンのインゴット製造に際し、シリコン粉末が有する問題点に鑑み、細粒のシリコンの粒径改善を図り、再利用を促進することによって、生産効率が高く、低価格化に対応した高純度の多結晶シリコンを製造する方法を提供することを目的としてなされたものである。

【0019】

【課題を解決するための手段】本発明は、下記の多結晶シリコンインゴットの製造方法を要旨としている。

【0020】すなわち、「シリコン粉末を高圧成形で造粒してのち、この造粒されたシリコン圧粉体を溶解原料としてインゴットを铸造することを特徴とする多結晶シリコンインゴットの製造方法」である。

【0021】上記の製造方法において、造粒されたシリコン圧粉体を乾燥または/および焼結するのが望ましく、さらに、溶解原料となるシリコン圧粉体の粒径を1 μm ~10 μm にするのが望ましい。

【0022】ここで、シリコン粉末には、流動造粒法によって発生する1 μm 未満のシリコン粉末および亜鉛還元法によって生成される多結晶シリコン粉末が含まれるが、これらの他に、製法の如何に関わらず、所定の純度を満足する直径1 μm 未満の細粒シリコンが対象となる。

【0023】

【発明の実施の形態】太陽電池用シリコンの製造においては、所定の光電変換効率を発揮する性能を具備するこ

とが前提となる。このため、太陽電池用に供される多結晶シリコンおよびこれを製造するためのシリコン原料には、これに必要な高純度、具体的にはそれぞれ6N(99.9999%)、7N(99.99999%)相当の純度を確保することが求められる。本発明では、粒径の細かなシリコン粉末であっても、このような高純度の多結晶シリコンを効率的に製造できるように、シリコン粉末を造粒し、これを溶解原料としてインゴットを鋳造することとしており、さらに、必要に応じて造粒されたシリコンを乾燥、焼結することを特徴としている。以下、その内容を説明する。

【0024】(1)シリコン粉末の造粒

シリコン粉末としては、流動造粒法によって製造される細粒の多結晶シリコンおよび亜鉛還元法で生成される多結晶シリコン粉が例示され、いずれも、直徑3μm以下の細粒のものである。シリコン粉末は1種または2種以上を、単独、または混合して使用することができる。いずれの場合にも、完全な均一混合にするのが望ましい。部分的なバラツキがあると、同一形状、寸法および密度比の圧粉体を製造した場合に、造粒後、または焼結後の寸法、特性が異なるからである。

【0025】図2は、本発明でシリコン粉末の造粒の際に使用した高圧ロール成形機の模式的な構成を示す図である。同図に示すように、均一に混合されたシリコン粉末1aは、加圧ロール2によって高圧成形され、造粒されたシリコン圧粉体1bとなる。

【0026】シリコン粉末の造粒には高圧成形が適する。シリコン粉末に高圧下で成形加工を施すことによって、粒子表面の凹凸部が相互の摩擦や押し合いによって崩壊し、または噛み合いによって粒子間にしっかりとした接触状況が作られるとともに、圧粉体の密度比を上昇することができるからである。

【0027】図2に示す高圧ロール成形機においては、充分に混合されたシリコン粉末1aに対し、加圧ロール2の圧下によって1T以上の圧力が加わった状態で成形される。成形されたシリコン圧粉体1bの粒径は、1mm~10mmにするのが望ましい。これは、圧粉体には空隙が多く伝熱が難いため、溶解性を確保するには粒径の上限を10mmとし、一方、溶解原料が細粒になりすぎると、溶融面上に浮遊するだけになるので、粒径の下限を1mmとするのが望ましいからである。

【0028】このとき、シリコン圧粉体の成形性(密度比等)が充分でない場合には、造粒バインダー、例えば、ポリビニールアルコール(PVA)が水溶液として添加される。添加割合は、シリコン圧粉体の成形性にもよるが、PVA濃度10%溶液をシリコン粉末に対して容積比10%にするのが望ましい。

【0029】造粒された後、シリコン圧粉体は溶解原料に供される。しかし、造粒の際にバインダーを添加した場合には、乾燥によって除去する必要がある。通常、脱

バインダーのための圧粉体の乾燥は、低温の予備乾燥と真空または減圧下での高温加熱の組み合わせによる。

【0030】造粒された圧粉体の強度が充分でなく、溶解原料のハンドリングに支障を生じる場合には、さらに焼結工程を追加するのが望ましい。前述の通り、シリコン粉末を常温で高圧成形して圧粉体を製造すると、圧粉体内の各粉末粒子間の結合は、主に機械的な噛み合いに基づくものであるから、その強度には限界がある。このため、圧粉体をさらに加熱し、粒子間に充分な原子的な結合を生じさせることによって、圧粉体の強度を確保することができる。

【0031】また、焼結によって、さらに粒子表面間の凝着現象が進展するので、嵩密度が上昇し熱伝導性が向上するので、シリコン原料の溶解において、溶解性を向上させることができる。

【0032】(2)インゴットの鋳造

図3は、本発明でシリコン圧粉体を溶解原料としてインゴットを連続鋳造する装置の概略構成を説明する図である。太陽電池用のシリコンインゴットの製造に際し、使用すべき装置として連続鋳造を限定するものではなく、鋳型を用いたバッチ式若しくは半連続式鋳造法でもよいが、本発明のように効率的なインゴット製造を意図する場合には、連続式鋳造装置を用いるのが望ましい。

【0033】図3に示す装置は電磁誘導による連続鋳造方式を採用しており、この方式では磁気圧によって坩堝7と溶融シリコン11とを無接触状態で保持して溶解できるので、2次汚染を回避できる。鋳造装置の外観は、水冷処理された気密容器3からなる。気密容器3内を真空排除できるように真空引き口4は真空排気ポンプと連結され、気密容器3内を不活性ガスを任意圧力で制御できるように不活性ガス口5が設けられている。また、この気密容器3は上部および下部を真空弁6に仕切られ、原料装入およびインゴットの取り出しを不活性雰囲気中でできるようになっている。

【0034】装置の中央部に金属製で無底形状の水冷式坩堝7が設けられ、その周囲に誘導コイル8が巻回し、誘導コイル8の下方には保温炉9が設置される。誘導コイル8中のインゴット10の上端部は溶解され、溶融シリコン11が形成される。原料装入器12の下方には原料ホッパーが設けられ、装入された粒状の溶解原料1bが旋回式の装入ダクトを介して溶融シリコンに供給される。この場合に、本発明で造粒されたシリコン圧粉体を投入することによって、溶解原料は溶融シリコンの表面に浮遊することなく、溶融シリコンに充分に溶け込み、均一に溶解することができる。さらに、不活性ガスの吹き出しやガス流れによって飛散することもない。保温炉9の下方には、引抜装置13が設けられており、シリコンインゴット10を所定の速度で連続して引き抜くようになっている。このようにして、シリコンインゴットを効率的に製造することができる。

【0035】

【実施例】本発明の効果を、実施例1、2に基づいて具体的に説明する。

【0036】(実施例1) 純度が7Nで、平均粒径が0.35μmのシリコン粉末を造粒し溶解原料として、シリコンインゴットを製造した。

【0037】a.造粒

シリコン粉末の造粒には、図2に示す高圧ロール成形機を用い、加圧ロールによる圧下は1Tとした。シリコン圧粉体の成形性を確保するため、シリコン粉末中にバイ

ンダーとしてPVA濃度10%の水溶液を容積比で10%添

加し、ミキサーにて均一に混合した。その後、高圧ロ

ール成形機の高圧成形によって、直径3～5mmのブリケ

ット(圧粉体)を製造した。

【0038】b.乾燥、焼結

脱バインダーをするため、ブリケットを乾燥した。乾燥条件は、乾燥機で200°C×10時間の予備乾燥をした後、

真空炉内(真空度は0.2Torr)で600°C×10hrとした。

【0039】乾燥後は、溶解原料として強度を確保するため、真空焼結炉を用いて、真空度10⁻⁴ Torrで、1300°C

×2時間の焼結を行った。

【0040】c.溶解

図3に示す連続鋳造装置によって、インゴットを製造した。気密容器内を真空排気した後、アルゴンガスを封入して+30Torrの圧力条件とした。坩堝の上方にある原料装入器の装入ダクトを横方向に退避させた状態で、図示しない発熱体を坩堝内に降下させ、インゴットの直上に接近配置して、誘導コイルに通電する。誘導コイル中のインゴットの上端面が溶解され、その上面に溶融シリコンが初期形成される。溶融シリコンを初期形成した後、造粒されたシリコン圧粉体を溶解原料として供給され、シリコン原料として溶解するとともに、保温炉内で徐々に凝固させて、引抜装置を作動させてシリコンインゴットを引き出す。

【0041】溶解時における原料装入では、圧粉体の強度が確保されており、ハンドリングにともなう原料の欠け、崩れ等の問題がなく、充分に溶解することができ、連続して鋳造装置の下方から、高純度の粉粒体状シリコンを取り出した。取り出したインゴットを分析したところ、純度は7N(99.99999%)であり、太陽電池用として適用できることを確認した。

【0042】(実施例2)亜鉛還元法で四塩化珪素を還元することによって生成される多結晶シリコン粉を造粒し溶解原料として、シリコンインゴットを製造した。生成されたシリコン粉末はいずれも直径3μm以下の細粒で、純度は7Nであった。

【0043】a.造粒

シリコン粉末中に、バインダーを混合させることなく、高圧ロール成形機の高圧成形によって、直径3～5mmのブリケット(圧粉体)を製造した。その他の造粒条件は、実施例1の場合と同様とした。

【0044】b.溶解

溶解時における原料装入では、ハンドリングにともなって若干の原料欠け、崩れが発生したが、溶融シリコン内で充分に溶解することができ、連続して鋳造装置の下方から、高純度の粉粒体状シリコンを取り出した。取り出したインゴットを分析したところ、純度は7N(99.99999%)であり、太陽電池用として問題のない品質であることを確認した。

【0045】

【発明の効果】本発明の多結晶シリコンの製造方法によれば、細粒のシリコン粉末であっても、溶解原料としての溶解性を損なうことなく使用することができるので、溶解原料のコストを上昇させることなく、品質的に安定して、太陽電池用基板として最適な高純度の多結晶シリコンを高い効率で製造することができる。

【図面の簡単な説明】

【図1】亜鉛還元法による多結晶シリコンの製造工程の一例を説明する図である。

【図2】本発明でシリコン粉末の造粒の際に使用した高圧ロール成形機の模式的な構成を示す図である。

【図3】本発明でシリコン圧粉体を溶解原料としてインゴットを連続鋳造する装置の概略構成を説明する図である。

【符号の説明】

1a:シリコン粉末、1b:シリコン圧粉体

2:加圧ロール、3:気密容器

4:真空引き口、5:不活性ガス口

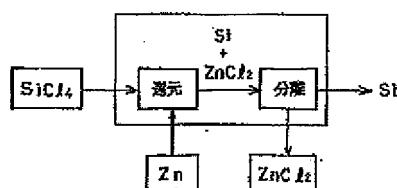
6:真空弁、7:坩堝

8:誘導コイル、9:保温炉

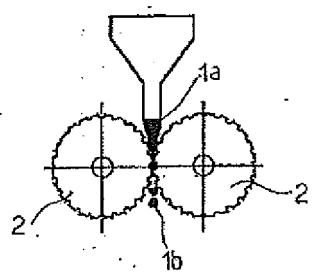
10:インゴット、11:溶融シリコン

12:原料装入器、13:引抜装置

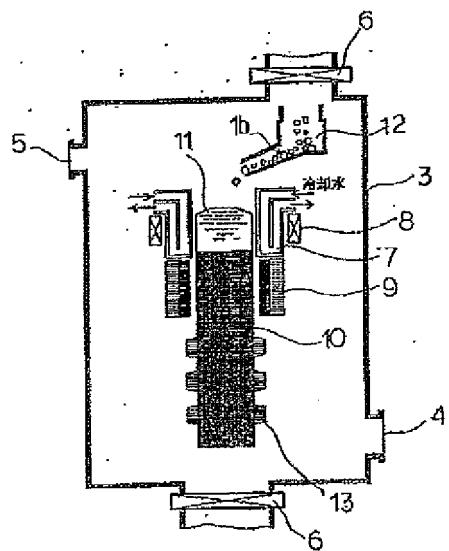
【図1】



【図2】



【図3】



*** NOTICES ***

**JPO and INPIT are not responsible for any
damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

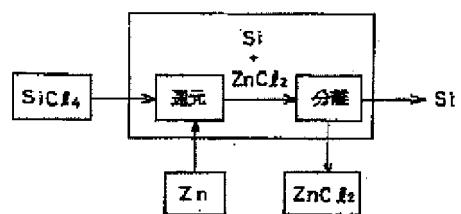
[Claim(s)]

[Claim 1]A manufacturing method of a polycrystal silicon ingot corning silicon powder by high-pressure molding, and casting an ingot by using as a dissolved raw material after and these silicon green compacts by which the granulation was carried out.

[Claim 2]A manufacturing method of the polycrystal silicon ingot according to claim 1 drying or/and sintering silicon green compacts by which the granulation was carried out.

[Claim 3]A manufacturing method of the polycrystal silicon ingot according to claim 1 or 2 particle diameter of silicon green compacts used as a dissolved raw material being 1 mm - 10 mm.

[Translation done.]



[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention concerns the silicon powder generated with manufacture of high purity silicon in more detail about the method of manufacturing the polycrystal silicon ingot used for solar cells, and relates to the manufacturing method of the polycrystal silicon ingot which uses this green compact as a dissolved raw material.

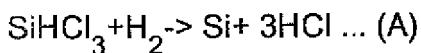
[0002]

[Description of the Prior Art] The production technology of a solar cell is applied in the silicon for semiconductors, an amorphous silicon, polycrystalline silicon, etc. and various fields with the spread of the latest photovoltaics, and technical development is remarkable also in which field. Although there was the characteristic required of the solar cell of the time of development by highly efficient-ization for the purpose of improvement in photoelectric conversion efficiency, it has come to point to low-pricing with the spread of solar cells. for this reason, the polycrystalline silicon manufactured by the raw material as silicon for semiconductors, for example in manufacture of a polycrystalline silicon board is non-standardized -- it comes to be used, carrying out crushing washing of elegance, the surplus material of single crystal silicon, etc. However, since the variety of the silicon for semiconductors covers a variety, or the thing of fixed quality is not securable, there is a limit also in low-pricing from the Reason of it being stabilized and being unable to secure quantity according to the quantity of production of the solar cell. For this reason, establishment of the quality of the high grade which demonstrates predetermined photoelectric conversion efficiency, and the production technology of the silicon corresponding to low-cost-izing is needed for development of a future solar cell.

[0003] Methods of manufacturing the polycrystalline silicon of a high grade from the former include the Siemens method (Siemens Method). This method is the method of returning the trichlorosilane (SiHCl_3) which is an intermediate compound by hydrogen (H_2). The trichlorosilane of the evaporated high grade is introduced in a reactor with hydrogen of a high grade, Trichlorosilane is made to decompose according to the reaction formula of following (A), and the surface of the polycrystalline silicon axis which supported

both ends with the graphite electrode and was heated by about 1100 ** is made to carry out vapor phase epitaxy of the polycrystalline silicon.

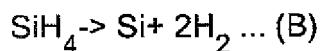
[0004]



However, in this Siemens method, since much electric power is consumed to heating of a polycrystalline silicon axis, power consumption worsens. Since only few ratios contribute to generation of polycrystalline silicon among the trichlorosilanes furthermore introduced into the reactor, productive efficiency is remarkably low. For this reason, this manufacturing method is not suitable as a manufacturing method of the silicon raw material for solar cells which points to low-pricing.

[0005]Then, the fluidized-bed-granulation method was developed as a process of generating completely different granular polycrystalline silicon from the Siemens method. In this manufacturing method, a fluid bed reactor is used, the silicon impalpable powder which is seeded in a reactor is made to flow, a mono silane (SiH_4) and the mixed gas of hydrogen are introduced into it, and a mono silane decomposes in the flow atmosphere heated by 600-700 **. At this time, granular polycrystalline silicon generates through the reaction formula of following (B).

[0006]



Since the gross area of granular silicon is overwhelmingly large compared with the silicon axis in the Siemens method, the production efficiency of the polycrystalline silicon within a fluid bed reactor is high. Although the purity of the polycrystalline silicon manufactured by the fluidized-bed-granulation method is equivalent compared with it of the Siemens method, it can reduce plant-and-equipment investment by half while being able to make 1/5 to about 1/10 reduce energy consumption. From such a viewpoint, it can be said that a fluidized-bed-granulation method is an effective method as a manufacturing method of the silicon raw material for solar cells.

[0007]What is called "a zinc reduction method of a silicon tetrachloride" (only henceforth a "zinc reduction method") has come to be adopted as a manufacturing method of the silicon raw material for solar cells as a manufacturing method of the polycrystalline silicon excellent in reaction efficiency. This manufacturing method is a method of manufacturing polycrystalline silicon, by returning this with molten zinc (Zn), using a silicon tetrachloride (SiCl_4) as an intermediate compound, as shown in the reaction formula of following

(C).

[0008]



Since a zinc reduction method is the method of carrying out reduction and decomposition and manufacturing, without carrying out secondary pollution of it after it carries out chloridation processing (halogenation reaction) of the metal silicon and generates an intermediate compound, as shown in the above-mentioned (C) formula, it is suitable for manufacture of high purity silicon. On the other hand, since almost all silicon tetrachlorides (SiCl_4) are the systems of reaction which advance to silicon (Si), it

excels in reaction efficiency, and it is a manufacturing method with sufficient productive efficiency, and is an advantageous manufacturing method also in the field of a manufacturing cost.

[0009] Drawing 1 is a figure explaining an example of the manufacturing process of the polycrystalline silicon by a zinc reduction method. In this zinc reduction method, it is roughly classified with the supply process of reaction raw materials ($SiCl_4$ and Zn), a reducing process, the partition process of a by-product, and the extraction process of high purity silicon (Si) so that clearly from the figure.

[0010] By a supply process, the metal zinc (Zn) which is the silicon tetrachloride ($SiCl_4$) and reducing agent which carried out chloridation processing of the metal silicon as a raw material is prepared in reaction raw materials. In order to make supply to a reactor easy, metal zinc (Zn) is heated by the range of 450-550 **, and is made into a molten state. On the other hand, the silicon tetrachloride ($SiCl_4$) which is an intermediate compound is accommodated at ordinary temperature, and is maintained at a liquid state (melting point-70 **).

[0011] In a reducing process, polycrystalline silicon and the subgenerated zinc chloride ($ZnCl_2$) are obtained by returning the silicon tetrachloride ($SiCl_4$) which is an intermediate compound with molten zinc (Zn). Since the boiling point of zinc chloride is 732 ** at this time, the zinc chloride ($ZnCl_2$) generated by the reduction reaction serves as a steam, The polycrystalline silicon powder generated simultaneously is dramatically detailed, and is discharged by the exterior of the reactor for reduction with the steam of zinc chloride ($ZnCl_2$).

[0012] In the partition process of a by-product, in order to separate the subgenerated zinc chloride ($ZnCl_2$), a vaporization separating method or a fluid filtration process is used. When using a vaporization separating method, the mixture which consists of polycrystalline silicon and zinc chloride ($ZnCl_2$) is introduced in a separation container, and is heated with vacuum suction after it, zinc chloride ($ZnCl_2$) is evaporated and separated, and polycrystalline silicon is collected. When using a fluid filtration process, it has the elevated-temperature characteristic in a separation container, and the fine ceramics filter of porosity with little contamination is given, and the introduced mixture is filtered under pressure.

[0013] In the extraction process of high purity silicon, by repeating the above-mentioned separation, an impurity is removed thoroughly and the fully high-grade-ized polycrystalline silicon is taken out. In this zinc reduction method, since the process of resulting in extraction of high purity silicon can be continuously processed from supply of the above-mentioned reaction raw materials, a manufacturing method with still higher productive efficiency can be provided.

[0014] Since it is a manufacturing method with high productive efficiency corresponding to low cost and a fluidized-bed-granulation method and a zinc reduction method moreover do not have fear of secondary pollution as above-mentioned, either, it is an effective method as a manufacturing method of the silicon raw material for solar cells.

[0015]

[Problem(s) to be Solved by the Invention] Usually, the granular polycrystalline silicon manufactured by a

fluidized-bed-granulation method is 100-1500 micrometers in diameter, and a pitch diameter is set to about 700 micrometers. It is generated by the fine grain by which it is generated at this time, for example, powder silicon 3 micrometers or less in diameter, about 15%. On the other hand, as above-mentioned, by a zinc reduction method, as shown in the aforementioned (C) formula, the polycrystalline silicon powder generated by returning a silicon tetrachloride with molten zinc is dramatically detailed, and each silicon taken out after separating a by-product is a thing of 3 micrometers or less in diameter a fine grain. [0016] Drawing 3 is a figure showing the outline composition of the continuous casting apparatus by the electromagnetic induction used for manufacture of the polycrystal silicon ingot mentioned later. The metal water-cooled crucible (cold crucible) which cut the segment at the center of the device so that it might be insulated electrically mutually is installed into the induction coil. And by making a magnetic field permeate in crucible, with magnetic pressure, melted silicon is held by no contacting and the dissolution is performed. In order to manufacture an ingot continuously, the upper bed side of the silicon ingot in an induction coil is dissolved, a granular dissolved raw material is supplied to the melted silicon formed in the upper surface, the dissolution and coagulation of a raw material are repeated, and a silicon ingot is pulled out caudad. During the raw material dissolution, it is maintained at an inert gas atmosphere after the vacuum suction in a device.

[0017] At this time, it only floats that the granular dissolved raw material supplied to melted silicon is 1 mm or less in a fine grain, for example, diameter, on the surface of melted silicon, and does not melt into melted silicon, and sufficient dissolution cannot be performed. And it disperses by blow off and the gas flow of inactive gas, and becomes a factor with poor gas suction in a device. Therefore, to use as a dissolved raw material granular polycrystalline silicon manufactured by a fluidized-bed-granulation method, it is necessary to remove fine grain silicon 1 mm or less in diameter. For this reason, the rise of dissolved raw material cost is not avoided. Since all the polycrystalline silicon powder generated by a zinc reduction method is fine grains 3 micrometers or less in diameter, it can be used with a continuous casting apparatus as shown in drawing 3.

[0018] This invention by aiming at the particle diameter improvement of the silicon of a fine grain, and promoting reuse in view of the problem which silicon powder has, on the occasion of ingot manufacture of the polycrystalline silicon in the conventional continuous casting process, Productive efficiency is high and is made for the purpose of providing the method of manufacturing the polycrystalline silicon of the high grade corresponding to low-pricing.

[0019]

[Means for Solving the Problem] This invention makes a gist a manufacturing method of the following polycrystal silicon ingot.

[0020] That is, it is "a manufacturing method of a polycrystal silicon ingot corning silicon powder by high-pressure molding, and casting an ingot by using as a dissolved raw material after and these silicon green compacts by which the granulation was carried out."

[0021] In the above-mentioned manufacturing method, it is desirable to dry or/and sinter silicon green compacts by which the granulation was carried out, and it is still more desirable for particle diameter of silicon green compacts used as a dissolved raw material to be 1 mm - 10 mm.

[0022]Here, although polycrystalline silicon powder generated by silicon powder and a zinc reduction method below 1 mm which are generated by a fluidized-bed-granulation method is contained in silicon powder, fine grain silicon with a diameter of less than 1 mm with which it is satisfied of predetermined purity [regardless of / a process] other than these is applicable.

[0023]

[Embodiment of the Invention]In manufacture of the silicon for solar cells, it will be the requisite to provide the performance which demonstrates predetermined photoelectric conversion efficiency. For this reason, the silicon raw material for manufacturing the polycrystalline silicon and this with which solar cells are presented is urged to secure a high grade required for this, and purity equivalent to 6N (99.9999%) and 7N (99.99999%) concrete respectively. In this invention, even if it is silicon powder with fine particle diameter, so that the polycrystalline silicon of such a high grade can be manufactured efficiently, Silicon powder is corned, and it supposes that an ingot is cast by making this into a dissolved raw material, and is characterized by drying and sintering further the silicon by which the granulation was carried out if needed. Hereafter, the contents are explained.

[0024](1) The polycrystalline silicon powder generated as granulation silicon powder of silicon powder by the polycrystalline silicon and the zinc reduction method of a fine grain which are manufactured by a fluidized-bed-granulation method is illustrated, and all are the things of 3 micrometers or less in diameter a fine grain. silicon powder -- one sort or two sorts or more -- independence -- or it can be mixed and used. It is desirable to use perfect homogeneous mixing in any case. It is because the size after a granulation or sintering differs from the characteristic when the green compact of identical shape, a size, and a density ratio is manufactured when there is partial variation.

[0025]Drawing 2 is a figure showing the typical composition of the high voltage roll forming machine used by this invention on the occasion of the granulation of silicon powder. As shown in the figure, high-pressure molding of the silicon powder 1a mixed uniformly is carried out by the pressure roll 2, and it serves as the silicon green compacts 1b by which the granulation was carried out.

[0026]High-pressure molding is suitable for the granulation of silicon powder. While the contact state which the uneven part of the particle surface collapsed by mutual friction and jam, or became brave by performing a fabricating operation to silicon powder under high voltage is made among particles by engagement, it is because the density ratio of a green compact can be gone up.

[0027]In the high voltage roll forming machine shown in drawing 2, to the fully mixed silicon powder 1a, where the pressure beyond 1T is added by pressing down of the pressure roll 2, it is fabricated. As for the particle diameter of the fabricated silicon green compacts 1b, it is desirable to use 1 mm - 10 mm. This is because it will become because it floats on a fusion face if the maximum of particle diameter shall be 10 mm for securing solubility, and a dissolved raw material becomes a fine grain too much on the other hand since [with many openings to a green compact] heat transfer is difficult, so it is desirable for the minimum of particle diameter to be 1 mm.

[0028]At this time, when the moldabilities (density ratio etc.) of silicon green compacts are not enough, a granulation binder (PVA), for example, poly vinyl alcohol, is added as solution. Although an addition rate is based also on the moldability of silicon green compacts, it is desirable to make a 10% of PVA

concentration solution into 10% of a volume ratio to silicon powder.

[0029]After a granulation is carried out, a dissolved raw material is presented with silicon green compacts. However, when a binder is added on the occasion of a granulation, desiccation needs to remove. Usually, desiccation of the green compact for a de binder is based on low-temperature predrying, a vacuum, or the combination of the heating at high temperature under decompression.

[0030]The intensity of the green compact by which the granulation was carried out is not enough, and when producing trouble in handling of a dissolved raw material, it is desirable to add a sintering process further. When high-pressure molding of the silicon powder is carried out at ordinary temperature and a green compact is manufactured as above-mentioned, since the combination between each powder particle in a green compact is due to mainly mechanical engagement, there is a limit in the intensity. For this reason, the intensity of a green compact is securable by heating a green compact further and producing atomic combination sufficient among particles.

[0031]Since bulk density goes up since the adhesion phenomenon between particle surfaces progresses further, and thermal conductivity improves by sintering, solubility can be improved in the dissolution of a silicon raw material.

[0032](2) Casting drawing 3 of an ingot is a figure explaining the outline composition of the device which carries out **** casting of the ingot by using silicon green compacts as a dissolved raw material by this invention. Although not the thing that limits continuous casting as a device which should be used but the batch type using a mold, or a half-continuous system casting process may be sufficient when manufacturing the silicon ingot for solar cells, when meaning efficient ingot manufacture like this invention, it is desirable to use a continuous system casting apparatus.

[0033]Since the device shown in drawing 3 has adopted the continuous casting method by electromagnetic induction, and it holds the crucible 7 and the melted silicon 11 by a non-contact state and it can be dissolved with magnetic pressure by this method, secondary pollution is avoidable. The appearance of a casting apparatus consists of the tight container 3 by which water cooling treatment was carried out. The vacuum suction mouth 4 is connected with an evacuation pump so that the vacuum exclusion of the inside of the tight container 3 can be carried out, and in the inside of the tight container 3, the inactive gas mouth 5 is formed so that inactive gas can be controlled by an arbitrary pressure. The upper part and the lower part are divided into the vacuum valve 6, and this tight container 3 has come to be able to perform extraction of raw material charging and an ingot in an inert atmosphere.

[0034]The no-bottom-shaped water cooling type crucible 7 is formed in the center section of the device by metal, and the heat insulation furnace 9 is installed in the circumference for the induction coil 8 under winding and the induction coil 8. The upper bed part of the ingot 10 in the induction coil 8 dissolves, and the melted silicon 11 is formed. A raw material hopper is formed under the raw-material-charging machine 12, and the inserted-in granular dissolved raw material 1b is supplied to melted silicon via a revolution-type insertion duct. In this case, it can fully dissolve in melted silicon at penetration and homogeneity, without a dissolved raw material floating on the surface of melted silicon by supplying the silicon green compacts by which the granulation was carried out by this invention. It does not disperse by blow off or the gas flow of inactive gas. Down the heat insulation furnace 9, the drawing apparatus 13 is

formed and the silicon ingot 10 is continuously drawn out at the rate of predetermined. Thus, a silicon ingot can be manufactured efficiently.

[0035]

[Example] The effect of this invention is concretely explained based on working example 1 and 2.

[0036] (Working example 1) By 7N, purity corned the silicon powder whose mean particle diameter is 0.35 micrometer, and manufactured the silicon ingot as a dissolved raw material.

[0037] a. Pressing down by a pressure roll was set to 1T at the granulation of granulation silicon powder using the high voltage roll forming machine shown in drawing 2. In order to secure the moldability of silicon green compacts, the solution of 10% of PVA concentration was added 10% by the volume ratio as a binder in silicon powder, and it mixed uniformly by the mixer. A briquette (green compact) 3-5 mm in diameter was manufactured by high-pressure molding of the high voltage roll forming machine after it.

[0038] b. The briquette was dried in order to carry out desiccation and a sintering de binder. After the drying condition carried out predrying of 200 **x 10 hours with the dryer, it was set to 600 **x10hr in the vacuum furnace (a degree of vacuum is 0.2Torr).

[0039] In order that after desiccation might secure intensity as a dissolved raw material, using the vacuum sintering furnace, it is degree-of-vacuum 10^{-4} Torr and performed sintering of 1300 **x 2 hours.

[0040] c. The ingot was manufactured with the continuous casting apparatus shown in dissolution drawing 3. After carrying out evacuation of the inside of a tight container, argon gas was enclosed and it was considered as the pressure conditions of +30Torr. Where the insertion duct of the raw-material-charging machine which is above crucible is evacuated to a transverse direction, the heating element which is not illustrated is dropped in crucible, approach arrangement is carried out right above an ingot, and it energizes to an induction coil. The upper bed side of the ingot in an induction coil is dissolved, and melted silicon is formed in the upper surface the first stage. After forming melted silicon the first stage, while the silicon green compacts by which the granulation was carried out are supplied as a dissolved raw material and dissolving as a silicon raw material, it is made to solidify gradually in a heat insulation furnace, a drawing apparatus is operated, and a silicon ingot is pulled out.

[0041] In the raw material charging at the time of the dissolution, the intensity of the green compact is secured, there are no problems, such as a chip of the raw material accompanying handling and collapse, it could fully dissolve, and the particulate matter-like silicon of the high grade was continuously taken out from the lower part of the casting apparatus. When the taken-out ingot was analyzed, purity is 7N (99.99999%) and it checked that it was applicable as an object for solar cells.

[0042] (Working example 2) The polycrystalline silicon powder generated by returning a silicon tetrachloride by a zinc reduction method was corned, and the silicon ingot was manufactured as a dissolved raw material. Each generated silicon powder was a fine grain 3 micrometers or less in diameter, and purity was 7N.

[0043] a. A briquette (green compact) 3-5 mm in diameter was manufactured by high-pressure molding of the high voltage roll forming machine, without mixing a binder in granulation silicon powder. Other granulation conditions presupposed that it is the same as that of the case of working example 1.

[0044] b. In the raw material charging at the time of the dissolution dissolution, although some raw

material chip and collapse occurred with handling, it could fully dissolve within melted silicon and the particulate matter-like silicon of the high grade was continuously taken out from the lower part of the casting apparatus. When the taken-out ingot was analyzed, it checked that purity was 7N (99.99999%) and was quality which is satisfactory as an object for solar cells.

[0045]

[Effect of the Invention] Since according to the manufacturing method of the polycrystalline silicon of this invention it can be used, without spoiling the solubility as a dissolved raw material even if it is the silicon powder of a fine grain, Without raising the cost of a dissolved raw material, it is stabilized in quality and the polycrystalline silicon of the high grade optimal as a substrate for solar cells can be manufactured at high efficiency.

[Translation done.]

* NOTICES *

**JPO and INPIT are not responsible for any
damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Industrial Application]This invention concerns the silicon powder generated with manufacture of high purity silicon in more detail about the method of manufacturing the polycrystal silicon ingot used for solar cells, and relates to the manufacturing method of the polycrystal silicon ingot which uses this green compact as a dissolved raw material.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

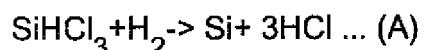
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] The production technology of a solar cell is applied in the silicon for semiconductors, an amorphous silicon, polycrystalline silicon, etc. and various fields with the spread of the latest photovoltaics, and technical development is remarkable also in which field. Although there was the characteristic required of the solar cell of the time of development by highly efficient-ization for the purpose of improvement in photoelectric conversion efficiency, it has come to point to low-pricing with the spread of solar cells. for this reason, the polycrystalline silicon manufactured by the raw material as silicon for semiconductors, for example in manufacture of a polycrystalline silicon board is non-standardized -- it comes to be used, carrying out crushing washing of elegance, the surplus material of single crystal silicon, etc. However, since the variety of the silicon for semiconductors covers a variety, or the thing of fixed quality is not securable, there is a limit also in low-pricing from the Reason of it being stabilized and being unable to secure quantity according to the quantity of production of the solar cell. For this reason, establishment of the quality of the high grade which demonstrates predetermined photoelectric conversion efficiency, and the production technology of the silicon corresponding to low-cost-izing is needed for development of a future solar cell.

[0003] Methods of manufacturing the polycrystalline silicon of a high grade from the former include the Siemens method (Siemens Method). This method is the method of returning the trichlorosilane (SiHCl_3) which is an intermediate compound by hydrogen (H_2). The trichlorosilane of the evaporated high grade is introduced in a reactor with hydrogen of a high grade, Trichlorosilane is made to decompose according to the reaction formula of following (A), and the surface of the polycrystalline silicon axis which supported both ends with the graphite electrode and was heated by about 1100 ** is made to carry out vapor phase epitaxy of the polycrystalline silicon.

[0004]

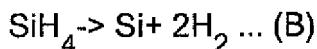


However, in this Siemens method, since much electric power is consumed to heating of a polycrystalline silicon axis, power consumption worsens. Since only few ratios contribute to generation of polycrystalline silicon among the trichlorosilanes furthermore introduced into the reactor, productive efficiency is

remarkably low. For this reason, this manufacturing method is not suitable as a manufacturing method of the silicon raw material for solar cells which points to low-pricing.

[0005]Then, the fluidized-bed-granulation method was developed as a process of generating completely different granular polycrystalline silicon from the Siemens method. In this manufacturing method, a fluid bed reactor is used, the silicon impalpable powder which is seeded in a reactor is made to flow, a mono silane (SiH_4) and the mixed gas of hydrogen are introduced into it, and a mono silane decomposes in the flow atmosphere heated by 600-700 **. At this time, granular polycrystalline silicon generates through the reaction formula of following (B).

[0006]



Since the gross area of granular silicon is overwhelmingly large compared with the silicon axis in the Siemens method, the production efficiency of the polycrystalline silicon within a fluid bed reactor is high. Although the purity of the polycrystalline silicon manufactured by the fluidized-bed-granulation method is equivalent compared with it of the Siemens method, it can reduce plant-and-equipment investment by half while being able to make 1/5 to about 1/10 reduce energy consumption. From such a viewpoint, it can be said that a fluidized-bed-granulation method is an effective method as a manufacturing method of the silicon raw material for solar cells.

[0007]What is called "a zinc reduction method of a silicon tetrachloride" (only henceforth a "zinc reduction method") has come to be adopted as a manufacturing method of the silicon raw material for solar cells as a manufacturing method of the polycrystalline silicon excellent in reaction efficiency. This manufacturing method is a method of manufacturing polycrystalline silicon, by returning this with molten zinc (Zn), using a silicon tetrachloride (SiCl_4) as an intermediate compound, as shown in the reaction formula of following (C).

[0008]



Since a zinc reduction method is the method of carrying out reduction and decomposition and manufacturing, without carrying out secondary pollution of it after it carries out chloridation processing (halogenation reaction) of the metal silicon and generates an intermediate compound, as shown in the above-mentioned (C) formula, it is suitable for manufacture of high purity silicon. On the other hand, since almost all silicon tetrachlorides (SiCl_4) are the systems of reaction which advance to silicon (Si), it excels in reaction efficiency, and it is a manufacturing method with sufficient productive efficiency, and is an advantageous manufacturing method also in the field of a manufacturing cost.

[0009]Drawing 1 is a figure explaining an example of the manufacturing process of the polycrystalline silicon by a zinc reduction method. In this zinc reduction method, it is roughly classified with the supply process of reaction raw materials (SiCl_4 and Zn), a reducing process, the partition process of a by-product, and the extraction process of high purity silicon (Si) so that clearly from the figure.

[0010]By a supply process, the metal zinc (Zn) which is the silicon tetrachloride (SiCl_4) and reducing

agent which carried out chloridation processing of the metal silicon as a raw material is prepared in reaction raw materials. In order to make supply to a reactor easy, metal zinc (Zn) is heated by the range of 450-550 **, and is made into a molten state. On the other hand, the silicon tetrachloride ($SiCl_4$) which is an intermediate compound is accommodated at ordinary temperature, and is maintained at a liquid state (melting point-70 **).

[0011]In a reducing process, polycrystalline silicon and the subgenerated zinc chloride ($ZnCl_2$) are obtained by returning the silicon tetrachloride ($SiCl_4$) which is an intermediate compound with molten zinc (Zn). Since the boiling point of zinc chloride is 732 ** at this time, the zinc chloride ($ZnCl_2$) generated by the reduction reaction serves as a steam, The polycrystalline silicon powder generated simultaneously is dramatically detailed, and is discharged by the exterior of the reactor for reduction with the steam of zinc chloride ($ZnCl_2$).

[0012]In the partition process of a by-product, in order to separate the subgenerated zinc chloride ($ZnCl_2$), a vaporization separating method or a fluid filtration process is used. When using a vaporization separating method, the mixture which consists of polycrystalline silicon and zinc chloride ($ZnCl_2$) is introduced in a separation container, and is heated with vacuum suction after it, zinc chloride ($ZnCl_2$) is evaporated and separated, and polycrystalline silicon is collected. When using a fluid filtration process, it has the elevated-temperature characteristic in a separation container, and the fine ceramics filter of porosity with little contamination is given, and the introduced mixture is filtered under pressure.

[0013]In the extraction process of high purity silicon, by repeating the above-mentioned separation, an impurity is removed thoroughly and the fully high-grade-ized polycrystalline silicon is taken out. In this zinc reduction method, since the process of resulting in extraction of high purity silicon can be continuously processed from supply of the above-mentioned reaction raw materials, a manufacturing method with still higher productive efficiency can be provided.

[0014]Since it is a manufacturing method with high productive efficiency corresponding to low cost and a fluidized-bed-granulation method and a zinc reduction method moreover do not have fear of secondary pollution as above-mentioned, either, it is an effective method as a manufacturing method of the silicon raw material for solar cells.

[Translation done.]

*** NOTICES ***

**JPO and iNPIT are not responsible for any
damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] Since according to the manufacturing method of the polycrystalline silicon of this invention it can be used, without spoiling the solubility as a dissolved raw material even if it is the silicon powder of a fine grain, Without raising the cost of a dissolved raw material, it is stabilized in quality and the polycrystalline silicon of the high grade optimal as a substrate for solar cells can be manufactured at high efficiency.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Usually, the granular polycrystalline silicon manufactured by a fluidized-bed-granulation method is 100-1500 micrometers in diameter, and a pitch diameter is set to about 700 micrometers. It is generated by the fine grain by which it is generated at this time, for example, powder silicon 3 micrometers or less in diameter, about 15%. On the other hand, as above-mentioned, by a zinc reduction method, as shown in the aforementioned (C) formula, the polycrystalline silicon powder generated by returning a silicon tetrachloride with molten zinc is dramatically detailed, and each silicon taken out after separating a by-product is a thing of 3 micrometers or less in diameter a fine grain.

[0016] Drawing 3 is a figure showing the outline composition of the continuous casting apparatus by the electromagnetic induction used for manufacture of the polycrystal silicon ingot mentioned later. The metal water-cooled crucible (cold crucible) which cut the segment at the center of the device so that it might be insulated electrically mutually is installed into the induction coil. And by making a magnetic field permeate in crucible, with magnetic pressure, melted silicon is held by no contacting and the dissolution is performed. In order to manufacture an ingot continuously, the upper bed side of the silicon ingot in an induction coil is dissolved, a granular dissolved raw material is supplied to the melted silicon formed in the upper surface, the dissolution and coagulation of a raw material are repeated, and a silicon ingot is pulled out caudad. During the raw material dissolution, it is maintained at an inert gas atmosphere after the vacuum suction in a device.

[0017] At this time, it only floats that the granular dissolved raw material supplied to melted silicon is 1 mm or less in a fine grain, for example, diameter, on the surface of melted silicon, and does not melt into melted silicon, and sufficient dissolution cannot be performed. And it disperses by blow off and the gas flow of inactive gas, and becomes a factor with poor gas suction in a device. Therefore, to use as a dissolved raw material granular polycrystalline silicon manufactured by a fluidized-bed-granulation method, it is necessary to remove fine grain silicon 1 mm or less in diameter. For this reason, the rise of dissolved raw material cost is not avoided. Since all the polycrystalline silicon powder generated by a zinc reduction method is fine grains 3 micrometers or less in diameter, it can be used with a continuous casting apparatus as shown in drawing 3.

[0018] This invention by aiming at the particle diameter improvement of the silicon of a fine grain, and

promoting reuse in view of the problem which silicon powder has, on the occasion of ingot manufacture of the polycrystalline silicon in the conventional continuous casting process, Productive efficiency is high and is made for the purpose of providing the method of manufacturing the polycrystalline silicon of the high grade corresponding to low-pricing.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] This invention makes a gist a manufacturing method of the following polycrystal silicon ingot.

[0020] That is, it is "a manufacturing method of a polycrystal silicon ingot corning silicon powder by high-pressure molding, and casting an ingot by using as a dissolved raw material after and these silicon green compacts by which the granulation was carried out."

[0021] In the above-mentioned manufacturing method, it is desirable to dry or/and sinter silicon green compacts by which the granulation was carried out, and it is still more desirable for particle diameter of silicon green compacts used as a dissolved raw material to be 1 mm - 10 mm.

[0022] Here, although polycrystalline silicon powder generated by silicon powder and a zinc reduction method below 1 mm which are generated by a fluidized-bed-granulation method is contained in silicon powder, fine grain silicon with a diameter of less than 1 mm with which it is satisfied of predetermined purity [regardless of / a process] other than these is applicable.

[0023]

[Embodiment of the Invention] In manufacture of the silicon for solar cells, it will be the requisite to provide the performance which demonstrates predetermined photoelectric conversion efficiency. For this reason, the silicon raw material for manufacturing the polycrystalline silicon and this with which solar cells are presented is urged to secure a high grade required for this, and purity equivalent to 6N (99.9999%) and 7N (99.99999%) concrete respectively. In this invention, even if it is silicon powder with fine particle diameter, so that the polycrystalline silicon of such a high grade can be manufactured efficiently, Silicon powder is corned, and it supposes that an ingot is cast by making this into a dissolved raw material, and is characterized by drying and sintering further the silicon by which the granulation was carried out if needed. Hereafter, the contents are explained.

[0024](1) The polycrystalline silicon powder generated as granulation silicon powder of silicon powder by the polycrystalline silicon and the zinc reduction method of a fine grain which are manufactured by a fluidized-bed-granulation method is illustrated, and all are the things of 3 micrometers or less in diameter a fine grain. silicon powder -- one sort or two sorts or more -- independence -- or it can be mixed and used. It is desirable to use perfect homogeneous mixing in any case. It is because the size after a

granulation or sintering differs from the characteristic when the green compact of identical shape, a size, and a density ratio is manufactured when there is partial variation.

[0025] Drawing 2 is a figure showing the typical composition of the high voltage roll forming machine used by this invention on the occasion of the granulation of silicon powder. As shown in the figure, high-pressure molding of the silicon powder 1a mixed uniformly is carried out by the pressure roll 2, and it serves as the silicon green compacts 1b by which the granulation was carried out.

[0026] High-pressure molding is suitable for the granulation of silicon powder. While the contact state which the uneven part of the particle surface collapsed by mutual friction and jam, or became brave by performing a fabricating operation to silicon powder under high voltage is made among particles by engagement, it is because the density ratio of a green compact can be gone up.

[0027] In the high voltage roll forming machine shown in drawing 2, to the fully mixed silicon powder 1a, where the pressure beyond 1T is added by pressing down of the pressure roll 2, it is fabricated. As for the particle diameter of the fabricated silicon green compacts 1b, it is desirable to use 1 mm - 10 mm. This is because it will become because it floats on a fusion face if the maximum of particle diameter shall be 10 mm for securing solubility, and a dissolved raw material becomes a fine grain too much on the other hand since [with many openings to a green compact] heat transfer is difficult, so it is desirable for the minimum of particle diameter to be 1 mm.

[0028] At this time, when the moldabilities (density ratio etc.) of silicon green compacts are not enough, a granulation binder (PVA), for example, poly vinyl alcohol, is added as solution. Although an addition rate is based also on the moldability of silicon green compacts, it is desirable to make a 10% of PVA concentration solution into 10% of a volume ratio to silicon powder.

[0029] After a granulation is carried out, a dissolved raw material is presented with silicon green compacts. However, when a binder is added on the occasion of a granulation, desiccation needs to remove. Usually, desiccation of the green compact for a de binder is based on low-temperature predrying, a vacuum, or the combination of the heating at high temperature under decompression.

[0030] The intensity of the green compact by which the granulation was carried out is not enough, and when producing trouble in handling of a dissolved raw material, it is desirable to add a sintering process further. When high-pressure molding of the silicon powder is carried out at ordinary temperature and a green compact is manufactured as above-mentioned, since the combination between each powder particle in a green compact is due to mainly mechanical engagement, there is a limit in the intensity. For this reason, the intensity of a green compact is securable by heating a green compact further and producing atomic combination sufficient among particles.

[0031] Since bulk density goes up since the adhesion phenomenon between particle surfaces progresses further, and thermal conductivity improves by sintering, solubility can be improved in the dissolution of a silicon raw material.

[0032] (2) Casting drawing 3 of an ingot is a figure explaining the outline composition of the device which carries out **** casting of the ingot by using silicon green compacts as a dissolved raw material by this invention. Although not the thing that limits continuous casting as a device which should be used but the batch type using a mold, or a half-continuous system casting process may be sufficient when

manufacturing the silicon ingot for solar cells, when meaning efficient ingot manufacture like this invention, it is desirable to use a continuous system casting apparatus.

[0033] Since the device shown in drawing 3 has adopted the continuous casting method by electromagnetic induction, and it holds the crucible 7 and the melted silicon 11 by a non-contact state and it can be dissolved with magnetic pressure by this method, secondary pollution is avoidable. The appearance of a casting apparatus consists of the tight container 3 by which water cooling treatment was carried out. The vacuum suction mouth 4 is connected with an evacuation pump so that the vacuum exclusion of the inside of the tight container 3 can be carried out, and in the inside of the tight container 3, the inactive gas mouth 5 is formed so that inactive gas can be controlled by an arbitrary pressure. The upper part and the lower part are divided into the vacuum valve 6, and this tight container 3 has come to be able to perform extraction of raw material charging and an ingot in an inert atmosphere.

[0034] The no-bottom-shaped water cooling type crucible 7 is formed in the center section of the device by metal, and the heat insulation furnace 9 is installed in the circumference for the induction coil 8 under winding and the induction coil 8. The upper bed part of the ingot 10 in the induction coil 8 dissolves, and the melted silicon 11 is formed. A raw material hopper is formed under the raw-material-charging machine 12, and the inserted-in granular dissolved raw material 1b is supplied to melted silicon via a revolution-type insertion duct. In this case, it can fully dissolve in melted silicon at penetration and homogeneity, without a dissolved raw material floating on the surface of melted silicon by supplying the silicon green compacts by which the granulation was carried out by this invention. It does not disperse by blow off or the gas flow of inactive gas. Down the heat insulation furnace 9, the drawing apparatus 13 is formed and the silicon ingot 10 is continuously drawn out at the rate of predetermined. Thus, a silicon ingot can be manufactured efficiently.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] The effect of this invention is concretely explained based on working example 1 and 2.

[0036] (Working example 1) By 7N, purity corned the silicon powder whose mean particle diameter is 0.35 micrometer, and manufactured the silicon ingot as a dissolved raw material.

[0037] a. Pressing down by a pressure roll was set to 1T at the granulation of granulation silicon powder using the high voltage roll forming machine shown in drawing 2. In order to secure the moldability of silicon green compacts, the solution of 10% of PVA concentration was added 10% by the volume ratio as a binder in silicon powder, and it mixed uniformly by the mixer. A briquette (green compact) 3-5 mm in diameter was manufactured by high-pressure molding of the high voltage roll forming machine after it.

[0038] b. The briquette was dried in order to carry out desiccation and a sintering de binder. After the drying condition carried out predrying of 200 **x 10 hours with the dryer, it was set to 600 **x10hr in the vacuum furnace (a degree of vacuum is 0.2Torr).

[0039] In order that after desiccation might secure intensity as a dissolved raw material, using the vacuum sintering furnace, it is degree-of-vacuum 10^{-4} Torr and performed sintering of 1300 **x 2 hours.

[0040] c. The ingot was manufactured with the continuous casting apparatus shown in dissolution drawing 3. After carrying out evacuation of the inside of a tight container, argon gas was enclosed and it was considered as the pressure conditions of +30Torr. Where the insertion duct of the raw-material-charging machine which is above crucible is evacuated to a transverse direction, the heating element which is not illustrated is dropped in crucible, approach arrangement is carried out right above an ingot, and it energizes to an induction coil. The upper bed side of the ingot in an induction coil is dissolved, and melted silicon is formed in the upper surface the first stage. After forming melted silicon the first stage, while the silicon green compacts by which the granulation was carried out are supplied as a dissolved raw material and dissolving as a silicon raw material, it is made to solidify gradually in a heat insulation furnace, a drawing apparatus is operated, and a silicon ingot is pulled out.

[0041] In the raw material charging at the time of the dissolution, the intensity of the green compact is secured, there are no problems, such as a chip of the raw material accompanying handling and collapse, it could fully dissolve, and the particulate matter-like silicon of the high grade was continuously taken out from the lower part of the casting apparatus. When the taken-out ingot was analyzed, purity is 7N

(99.99999%) and it checked that it was applicable as an object for solar cells.

[0042](Working example 2) The polycrystalline silicon powder generated by returning a silicon tetrachloride by a zinc reduction method was corned, and the silicon ingot was manufactured as a dissolved raw material. Each generated silicon powder was a fine grain 3 micrometers or less in diameter, and purity was 7N.

[0043]a. A briquette (green compact) 3-5 mm in diameter was manufactured by high-pressure molding of the high voltage roll forming machine, without mixing a binder in granulation silicon powder. Other granulation conditions presupposed that it is the same as that of the case of working example 1.

[0044]b. In the raw material charging at the time of the dissolution dissolution, although some raw material chip and collapse occurred with handling, it could fully dissolve within melted silicon and the particulate matter-like silicon of the high grade was continuously taken out from the lower part of the casting apparatus. When the taken-out ingot was analyzed, it checked that purity was 7N (99.99999%) and was quality which is satisfactory as an object for solar cells.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a figure explaining an example of the manufacturing process of the polycrystalline silicon by a zinc reduction method.

[Drawing 2] It is a figure showing the typical composition of the high voltage roll forming machine used by this invention on the occasion of the granulation of silicon powder.

[Drawing 3] It is a figure explaining the outline composition of the device which carries out **** casting of the ingot by using silicon green compacts as a dissolved raw material by this invention.

[Description of Notations]

- 1a: Silicon powder and 1b : silicon green compacts
- 2: A pressure roll and 3 : tight container
- 4: A vacuum suction mouth and 5 : inactive gas mouth
- 6: A vacuum valve and 7 : crucible
- 8: An induction coil and 9 : heat insulation furnace
- 10: An ingot and 11 : melted silicon
- 12: A raw-material-charging machine and 13 : drawing apparatus

[Translation done.]

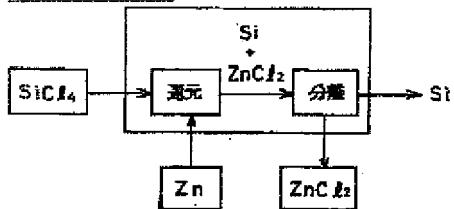
* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

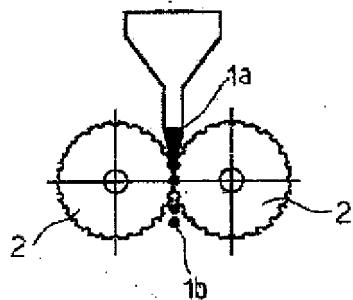
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

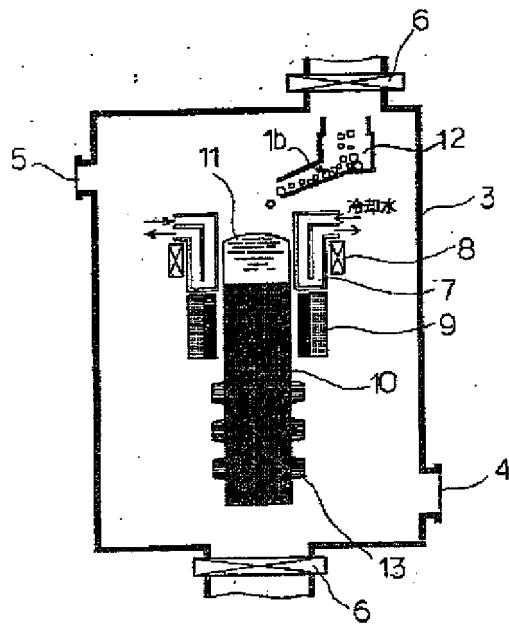
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]